

PRODUCTION OF HYDROBROMIC ACID FROM BROMINE AND METHANE FOR HYDROGEN PRODUCTION

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Abstract

A cooperative program between Sandia National Laboratories (SNL) and the SRT Group was recently begun to advance the development of a chemical process to produce hydrobromic acid from bromine and methane. The purpose of the SNL program is to provide fundamental reaction kinetics information that will constitute the basis for system engineering by SRT. The SNL activities consist of computational chemistry and laboratory experimentation. Preliminary calculations of chemical equilibrium behavior and reaction kinetics were performed using the CHEMKIN computer program and its associated thermodynamic and kinetic databases. Calculations were performed for reactions involving the bromine-methane and bromine-methane-steam systems. The equilibrium conversion of bromine to HBr in the two processes is excellent, especially at temperatures below 900K. If equilibrium is achieved in the bromine-methane process, then the other principal product is solid carbon in some form, e.g., coke or soot. If solid carbon is not produced, then the reactor effluent may contain significant amounts of brominated hydrocarbons. From a purely thermodynamic point of view, the bromine-methane-steam process appears to be more attractive because the carbon in methane is converted almost completely into carbon dioxide.

Introduction

A hydrogen production process that requires the formation of hydrobromic acid as one of the primary steps has been proposed by the SRT Group, Inc., Miami, FL. SRT has described the process and preliminary development studies in detail elsewhere, so only the basic features are given here [Schleif 1997, SRT Group 1998]. The initial step in the process is the formation of hydrobromic acid from bromine and a hydrocarbon, e.g., methane. This reaction is conducted at elevated temperature, as high as 800°C. An alternative reaction scheme includes steam among the reactants to convert the carbon in the feedstock to carbon dioxide rather than solid carbon. The HBr generated in the reactor is collected with water to produce a concentrated solution of HBr that is electrolyzed in a separate process step, yielding hydrogen and bromine. The latter constituent is recycled to the reactor to perpetuate the HBr production cycle. The hydrogen is available for generating energy by various means. Alternatively, both constituents may be used to produce electrical power via a regenerative hydrogen-bromine fuel cell of a proprietary design.

A cooperative program between Sandia National Laboratories (SNL) and the SRT Group was recently begun to advance the development of the chemical process to produce hydrobromic acid. The purpose of the SNL participation is to determine fundamental reaction rate equations that will constitute the basis for reactor engineering by SRT. The SNL work consists of several activities. The primary SNL activity in the initial phase of this project is to employ computer modeling of chemical reaction kinetics to determine the reaction rate equations. Computation will be used to evaluate the equilibria of the various reactions studied in order to predict the extent of the desired reaction and the formation of by-products. Another activity is to conduct laboratory experiments to determine the fundamental characteristics of a number of chemical reactions that produce hydrobromic acid from hydrocarbon precursors.

Calculations of both chemical equilibrium behavior and reaction kinetics are required to interpret the laboratory reactor data. These calculations will be performed using the CHEMKIN computer program and its associated thermodynamic and kinetic databases. Additional information may need to be input to complete the database for computations. The results of the laboratory experiments will be compared with the predictions of the computations to refine the reaction rate equations. The equilibrium calculations will enable the experimental apparatus to be designed with full regard for all of the reaction products that may be formed. Such calculations also provide useful information regarding the energetics of the reactions which is useful for engineering design.

This report summarizes the status of the Sandia National Laboratories segment of this project during the startup period of February 2001 through April 2001. The planned future work is also discussed.

Computational Chemistry of Bromine-Methane Reactions

This section summarizes the calculations that have been carried out to determine the feasibility of producing hydrogen bromide from bromine, methane, and (optionally) steam. As is customary in such investigations, the process is first examined from a thermodynamic point of view to determine if it is viable. If it is, then kinetic simulations are carried out to estimate whether the time scales are reasonable. It must be emphasized that the results presented here are tentative

because the chemical mechanisms are almost certainly incomplete, some of the data are of uncertain accuracy, and a detailed parameter study has not been performed at this stage of the project. The results presented here are useful mainly as a guide for companion experiments that are to be conducted at SNL in the upcoming months. The results of these experiments should allow the models to be refined to the point that they can be used with confidence in detailed reactor simulations.

Data Collection

Two primary sources were used to assemble the gas-phase mechanism and data needed for the calculations. The species and reactions involved in methane pyrolysis and combustion were taken from GRI-Mech Version 1.2, and the corresponding thermodynamic data file was used as the default. Reactions and thermodynamic data for bromine-containing species were obtained from a NIST Web site [NIST 2001]. Several reactions tabulated by Babushok [1996] but not included in the NIST website (perhaps because of uncertain accuracy) were added to our compilation. About a dozen miscellaneous reactions from various sources were also added, partly to provide a pathway for complete bromination of methane. Thermodynamic data for all bromomethanes and bromomethyl radicals were obtained by fitting the values reported by Paddison and Tschuikow-Roux [1998] to complement the NIST database. An approximate entry for carbonyl bromide (COBr_2) was constructed by using handbook values of the enthalpy, entropy, and heat capacity at 298K [Dean 1973]. This value was used only for the equilibrium calculations, as a means of demonstrating that this species would not be present in significant amounts. Thus, a more accurate entry was not required.

Equilibrium Calculations

The first step is to perform a purely thermodynamic analysis to determine the species present in the system at equilibrium. The results are a function of the prevailing temperature and pressure, which is taken to be 1 atm. The computations have been carried out using the Sandia EQUIL code, which is basically a CHEMKIN interface to the well-known STANJAN code. The results have been checked against a spreadsheet-based calculation at 298K and the predictions of the online solver EQUILIB-Web [Ecole Polytechnique Montreal 2001]. Both STANJAN and EQUILIB-Web have certain advantages: the latter automatically, and almost effortlessly, gives the global equilibrium composition by including every species in its database, while the former allows one to perform partial equilibrium calculations by including only those species that are of interest. We have used STANJAN here in order to take advantage of its flexibility.

For the system in which bromine and methane are the reactants, the primary reaction is



where C(s) is solid carbon (graphite). This stoichiometry was input to STANJAN, and the results are shown in Figure 1. Note that the ordinate is the *overall* mole fraction, on a logarithmic scale, with both gaseous and solid constituents included. Clearly, the conversion of methane to carbon is essentially complete; the formation of HBr is also nearly complete at low temperatures, but at higher temperatures HBr begins to dissociate into H_2 and Br_2 , and eventually Br_2 itself begins to dissociate. No brominated hydrocarbons are formed under these circumstances.

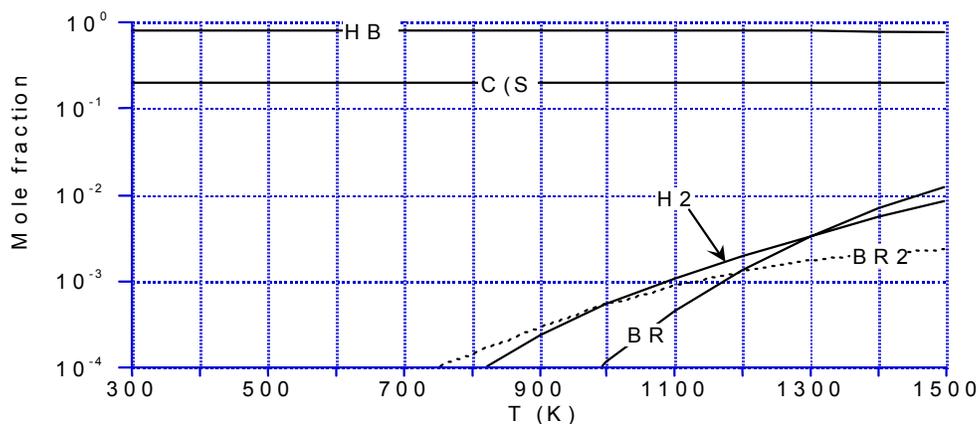


Fig 1. Equilibrium composition $\text{CH}_4 + 2 \text{BR}_2$ from STANJAN

The rate of formation of solid carbon must depend on the surface-to-volume ratio in the reactor, where the surface may include more than just the reactor walls. Therefore, it is possible that carbon deposition may not actually occur to a significant extent under some conditions of practical interest. Because of this, it is useful to carry out partial equilibrium calculations in which solid carbon has been deleted. Performing this calculation, using the list of species involved in the mechanism described above, yields the results shown in Figure 2. Obviously, the situation is now far more complicated. HBr is still the dominant species in the gas, but there is a significant amount of free Br_2 , even at relatively low temperatures, and the carbon is distributed among a wide variety of bromocarbons and hydrocarbons. For kinetic simulations in which solid carbon is not included, we might well expect these same gaseous species to appear. However, it must be emphasized that partial equilibrium calculations must be interpreted cautiously because the results are entirely dependent on the list of species that one chooses to include.

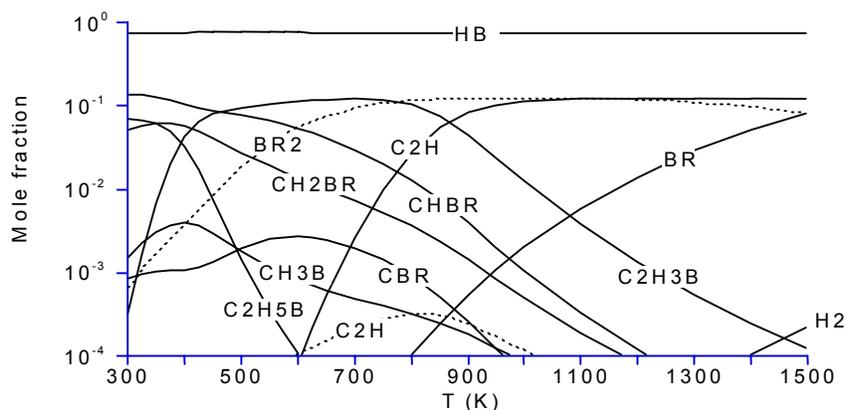


Fig 2. Equilibrium composition for $\text{CH}_4 + 2\text{BR}_2$ from STANJAN (solid carbon not included)

For the system in which H₂O is a reactant, the ideal reaction would be



This stoichiometry was used in additional equilibrium calculations, and the unconstrained results are shown in Figure 3. As before, the ideal product mix is obtained at low temperatures, but significant amounts of by-products begin to appear as T increases. In this case, however, solid carbon is basically absent, so it will not be necessary to deal with the complications involved with heterogeneous reactions. It should also be noted that carbonyl bromide, COBr₂, a highly hazardous substance, is not predicted to form in significant quantities, at least at equilibrium.

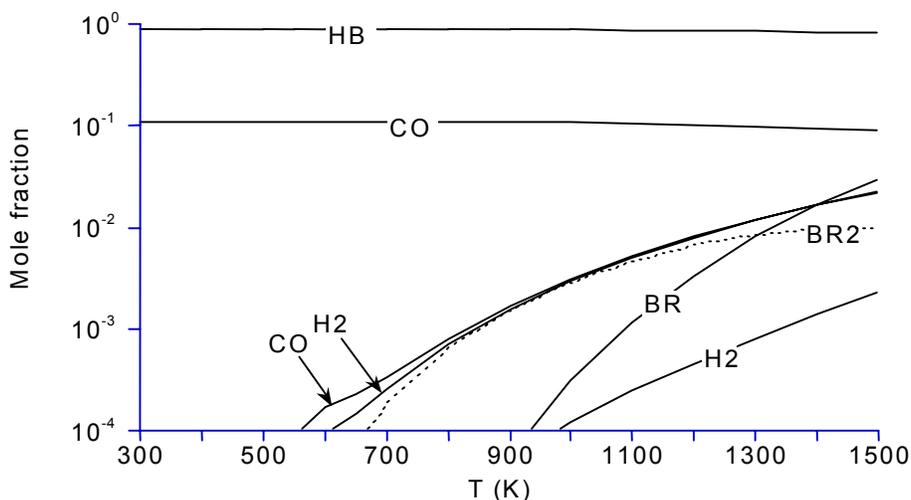


Fig 3. Equilibrium composition for CH₄ + 4BR₂ + 2H₂O from STANJAN

Kinetic Calculations

In order to determine whether the equilibrium compositions computed above can actually be achieved, time-dependent reactor simulations were carried out using the full kinetic mechanism described above. At this point there is nothing to be gained by choosing any particular reactor configuration, so we used the Sandia plug-flow reactor code PLUG; the batch-reactor code SENKIN would almost certainly give very similar results. PLUG is a steady-state code, but the residence time in the reactor assumes the role of the actual time in a transient code. For each set of reactants, the simulation has been carried out for only one or two sets of conditions, so the results are obviously only suggestive.

As mentioned previously, the chemical mechanism does not yet include deposition of solid carbon from the various possible gas-phase precursors. If it did, then the surface-to-volume ratio would become a key parameter. In principle this is easy to remedy, but it is unlikely that the reactive sticking coefficients for most of the gas-phase species have been measured, and the reaction products themselves are probably not known. If experiments show that carbon is

deposited in significant amounts, then the mechanism will obviously have to be augmented. In the meantime, simulations have been carried out for the gas phase alone. With regard to this issue, we note that laboratory tests by SRT resulted in formation of solid carbon for reactions of the bromine-methane-steam system when bromine and steam were present in stoichiometric excess [SRT Group 1998].

A sample set of kinetic results for the bromine-methane system is shown in Figure 4. In this figure, the concentrations of various species are plotted vs. a logarithmic time scale. The initial temperature is specified as 873K, but the reactor is adiabatic, so the temperature will vary as a function of time. The resulting temperature profile is as shown in Figure 5. From Figure 4 it can be concluded that the dominant overall reaction in the first phase of the process is formation of dibromomethane,



This is obviously very exothermic and is essentially complete within 0.01 s. Some CH_3Br is formed as well. At longer times, the CH_2Br_2 is replaced to some extent first by CHBr_3 and then by the unsaturated compounds $\text{C}_2\text{H}_3\text{Br}$ and C_2H_2 , formed endothermically. However, it is clear that the process has not reached equilibrium even after 10^4 s, so the final composition does not quite match that given in Figure 2 for the final temperature of 945K. In any case, the large concentration of brominated hydrocarbons is a cause for concern, and it will be crucial to determine whether deposition of solid carbon can prevent the formation of these compounds.

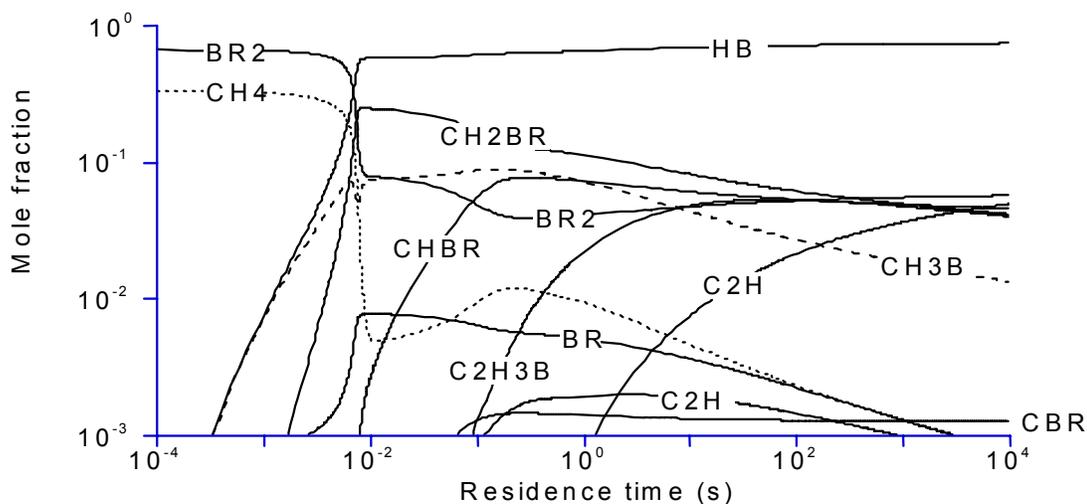


Fig 4. Kinetics for $\text{CH}_4 + 2\text{Br}_2$ (Adiabatic, initial $T = 873$ K, no solid carbon)

Representative kinetic results for the bromine-methane-steam system are shown in Figures 6 and 7. In this case the initial temperature is somewhat higher (1000K), but the reactor is again adiabatic. The process now appears to take place in three distinct stages. At about 0.001 s, Reaction (3) noted above goes to completion, thereby consuming all of the CH_4 and half of the available Br_2 . This step is significantly exothermic and leaves a mixture containing equal

amounts of Br_2 , H_2O , and HBr , and half this amount of CH_2Br_2 . At times on the order of 1 s, CH_2Br_2 is largely replaced by the more heavily brominated species CHBr_3 , and some CBr_4 . This reaction consumes additional Br_2 and releases hydrogen to form more HBr . It can be seen that the associated heat effect is only slight. However, a true combustion process finally ignites at about 300 s, rapidly pushing the temperature to its final value of 1534K. All of the hydrocarbons (brominated or otherwise) are destroyed to yield CO_2 and CO , and the final composition is just as predicted by Figure 3.

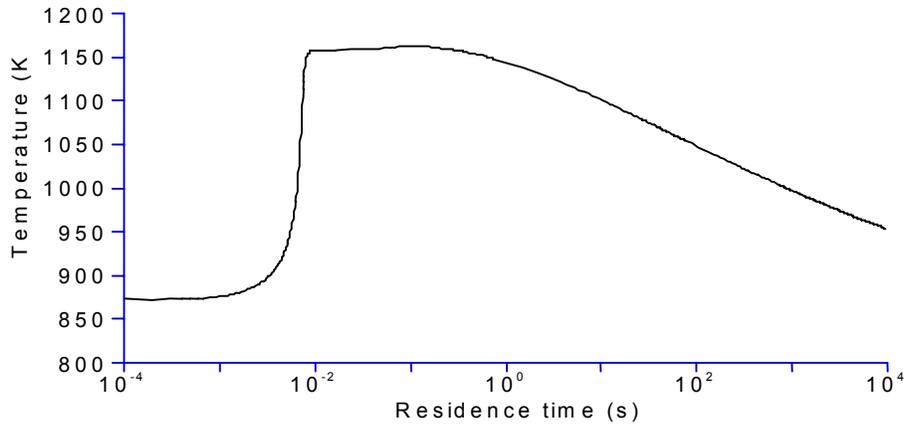


Fig 5. Temperature history for $\text{CH}_4 + 2\text{BR}_2$ (Adiabatic, initial $T = 873 \text{ K}$, no solid carbon)

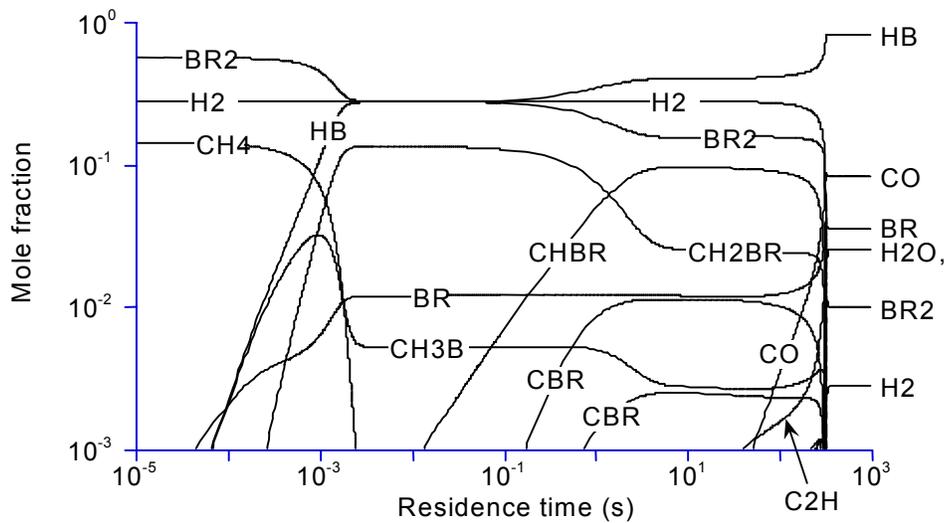
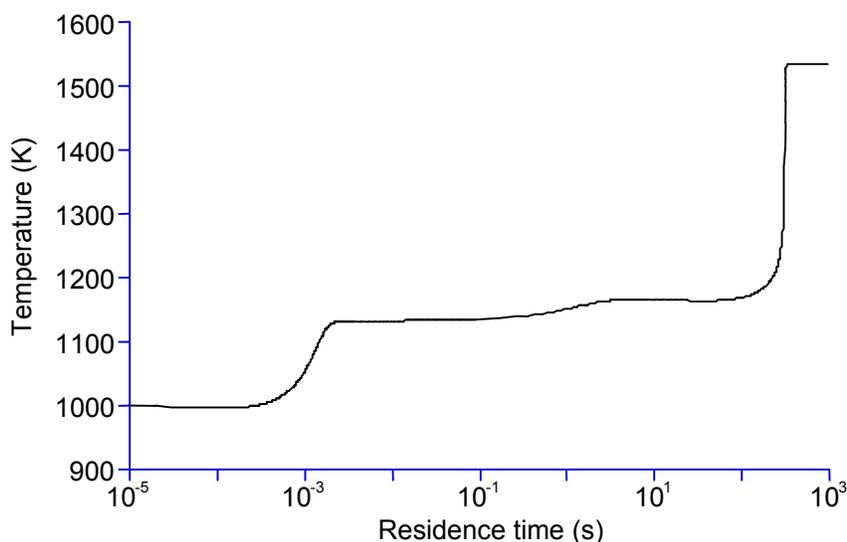


Fig 6. Kinetics for $\text{CH}_4 + 4\text{BR}_2 + 2\text{H}_2\text{O}$ (Adiabatic, initial $T = 1000 \text{ K}$, no solid carbon)



**Fig 7. Temperature history for $\text{CH}_4 + 4 \text{BR}_2 + 2 \text{H}_2\text{O}$
(Adiabatic, initial T = 1000 K, no solid carbon)**

Conclusions

The equilibrium conversion of Br_2 to HBr in the two processes is excellent, especially at low temperatures. If equilibrium is achieved in the bromine-methane process, then the other principal product is solid carbon in some form, e.g., coke or soot. If solid carbon is not produced, then the effluent gas will almost certainly contain significant amounts of brominated hydrocarbons. Not only do these toxic substances present a disposal problem, but they represent a loss of bromine from the system and an incomplete use of the hydrogen introduced in methane. From a purely thermodynamic point of view, the steam process appears to be more attractive, as the carbon in methane is converted almost completely into easily handled CO_2 . However, the kinetics for the steam process are not very encouraging. The residence time required for complete combustion of the carbon is about 350 sec., which would seem to be impracticably long. Of course, the process could be accelerated by using a higher initial temperature.

Future Work

Laboratory experiments will be conducted to provide data that can be used to develop the chemical kinetics equation, rather than demonstrate the process as it might be used in production. An experimental reactor will be designed and constructed to allow a broad envelope of reaction conditions to be evaluated. The most important variables that define this envelope are the reactor temperature, the ratios of the reactants in the feedstock, and the residence time in the reactor. The laboratory reactor will be configured to investigate the reactions of methane with bromine initially and to progress to a study of the reactions that occur when water vapor is present. The extent and rate of the reactions will be determined by analysis of both gaseous and condensed products from the reactor effluent. Analytical techniques will be employed that are suitable for

quantification of the range of brominated hydrocarbons which may form. These techniques include both on-line gas chromatography and off-line analysis. Condensed products will be analyzed by chemical titration and infrared spectroscopy. Other analytical methods will be used as necessary to obtain definitive data.

As part of the continuing computational chemistry effort, the addition of carbon deposition reactions to the mechanism for the bromine-methane process and, possibly, the bromine-methane-steam process is the most significant step that could be taken to obtain a more complete picture of the options for HBr production. However, it is probably not worth pursuing this activity until experiments show that solid carbon forms under conditions of practical interest. It should also be acknowledged that there are several other sources of uncertainty in the calculations, even for the bromine-methane-steam process. First, there is no doubt that the gas-phase reaction mechanism as it stands is incomplete, in part because it has been assembled largely from two independently constructed sub-mechanisms, bromocarbon chemistry and hydrocarbon combustion. It is possible that there are reaction steps for direct bromocarbon combustion that could alter the overall kinetics. In addition, many of the reactions involving bromocarbons have been investigated from the point of view of atmospheric chemistry, so their rates have not been measured at the elevated temperatures of interest for process development. Arrhenius extrapolation of these rates to much higher temperatures is somewhat uncertain, but in the present case there is no alternative. For all of these reasons, the experiments being planned at SNL should provide extremely useful information for model development and refinement.

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